

PARAFFIN AND NAPHTHENE DISTRIBUTION BY CARBON NUMBER OF SATURATED PETROLEUM DISTILLATES BY GC

UOP Method 741-86

SCOPE

This method is for determining the distribution of paraffins and naphthenes by carbon number, in hydrocarbon samples having an endpoint of 200 C or less (C₃-C₁₁). C₁₂'s at concentrations less than 3% can be determined. Olefins and aromatics interfere and must be removed prior to analysis by ASTM Method D 2002, D 2003 or other suitable technique. The lower limit of detection for a single carbon number hydrocarbon type is 0.05 mass- or LV-%.

OUTLINE OF METHOD

The sample is injected into a gas chromatograph that is equipped with a column packed with treated molecular sieves. Internal normalization of peak areas after correction for differences in response is used to obtain a distribution of the components.

APPARATUS

Balance, readability 0.1-mg

Chromatographic column, 1.6 m of 2-mm ID (1/8-inch OD) stainless steel tubing packed with specially treated 13X molecular sieves, Analytical Controls Inc., Part No. 50.06.530, or equivalent

Gas Chromatograph, capable of column temperature programming to 400 C and equipped with a flame ionization detector. The detector must be capable of producing a minimum peak height response of 30 μ V for 0.1% of *n*-heptane when operated at the stated conditions. Background noise at these conditions is not to exceed 3 μ V.

Integrator, electronic, or equivalent equipment for obtaining peak areas

Oxygen remover, Oxy-Trap, Alltech Associates, Cat. No. 4001, or equivalent. An oxygen remover in the carrier gas line ensures optimum column life.

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

Recorder, 1-mV full scale, 1-sec or less full-scale response

Regulator, air, two-stage, high purity, Matheson, Model 3104-590, or equivalent

Regulator, hydrogen, two-stage, high purity, Matheson Model 3104-350, or equivalent

Regulator, nitrogen, two-stage, high purity, Matheson Model 3104-580, or equivalent

Sample injector, any syringe or injection system capable of introducing a 0.2- μ L volume of sample, such as a Hamilton 701-NWG syringe, Alltech Associates, or equivalent

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified.

Air, total hydrocarbons less than 2.0 ppm as methane (zero gas)

n-Butylcyclohexane, 99% purity, Wiley Organics, Cat. No. 0419.70, or equivalent (C₁₀ naphthene)

Cyclohexane, 99.9% purity, Wiley Organics, Cat. No. 0679.02, or equivalent (C₆ naphthene)

n-Decane, 99.9% purity, Wiley Organics, Cat. No. 0812.5 or equivalent (C₁₀ paraffin)

Ethylcyclohexane, 99.9% purity, Wiley Organics, Cat. No. 2442.00, or equivalent (C₈ naphthene)

n-Heptane, 99.9% purity, Wiley Organics, Cat. No. 3111.00, or equivalent (C₇ paraffin)

n-Hexane, 99.9% purity, Wiley Organics, Cat. No. 3442.00, or equivalent (C₆ paraffin)

Hydrogen, 99.95% minimum purity, total hydrocarbons less than 0.5 ppm as methane (zero gas)

Isopropylcyclohexane, 99.7% purity, Wiley Organics, Cat. No. 8260.52, or equivalent (C₉ naphthene)

Methylcyclohexane, 99.9% purity, Wiley Organics, Cat. No. 4082.00, or equivalent (C₇ naphthene)

Nitrogen, 99.9% minimum purity, total hydrocarbons less than 0.5 ppm as methane (zero gas)

n-Nonane, 99.5% purity, Wiley Organics, Cat. No. 6782.00, or equivalent (C₉ paraffin)

n-Octane, 99.9% purity, Wiley Organics, Cat. No. 7056.50, or equivalent (C₈ paraffin)

Pentylcyclohexane, 99% purity, Wiley Organics, Cat. No. 7500.00, or equivalent (C₁₁ naphthene)

n-Undecane, 99.7% purity, Wiley Organics, Cat. No. 9480.00, or equivalent (C₁₁ paraffin)

PROCEDURE

Install the oxygen remover in the supply line between the hydrogen source and the carrier gas inlet on the gas chromatograph.

The operating conditions for the analysis are given in Table 1.

Table 1
Operating Conditions

Carrier gas	hydrogen
Carrier gas flow rate	15 mL/min
Detector	flame ionization
Detector temperature	250 C
Injection port temperature	250 C
Hydrogen flow rate*	15 mL/min
Air flow rate*	400 mL/min
Makeup gas	nitrogen
Makeup flow rate*	30 mL/min
Column temperature program	
Initial temperature	100 C
Programming rate	6 C/min
Final temperature	400 C
Chart speed	0.5 cm/min
Sample size	0.2 μL

* Consult the manufacturer's instrument manual for suggested flow rates

Chromatographic Technique

Install the chromatographic column and establish the flow rates and operating temperatures specified under *Operating Conditions*. **CAUTION:** Leakage of hydrogen into the confined volume of the column compartment can cause a violent explosion. It is, therefore, mandatory to test for leaks each time a connection is made and periodically thereafter. Condition the column at 100 C for one hour then program up to 400 C at 6 C/min. Hold the column temperature at 400 C until a stable recorder baseline is established at the required sensitivity. Cool the column oven to 100 C. Inject a sample into the gas chromatograph and immediately start the temperature programmer, integrator and recorder. Identify each hydrocarbon type from the typical chromatograms shown in Figs. 1 and 2 and by comparison with the calibration blend, see *Calibration*. Separate incompletely resolved hydrocarbon types with a vertical line as shown in the figures.

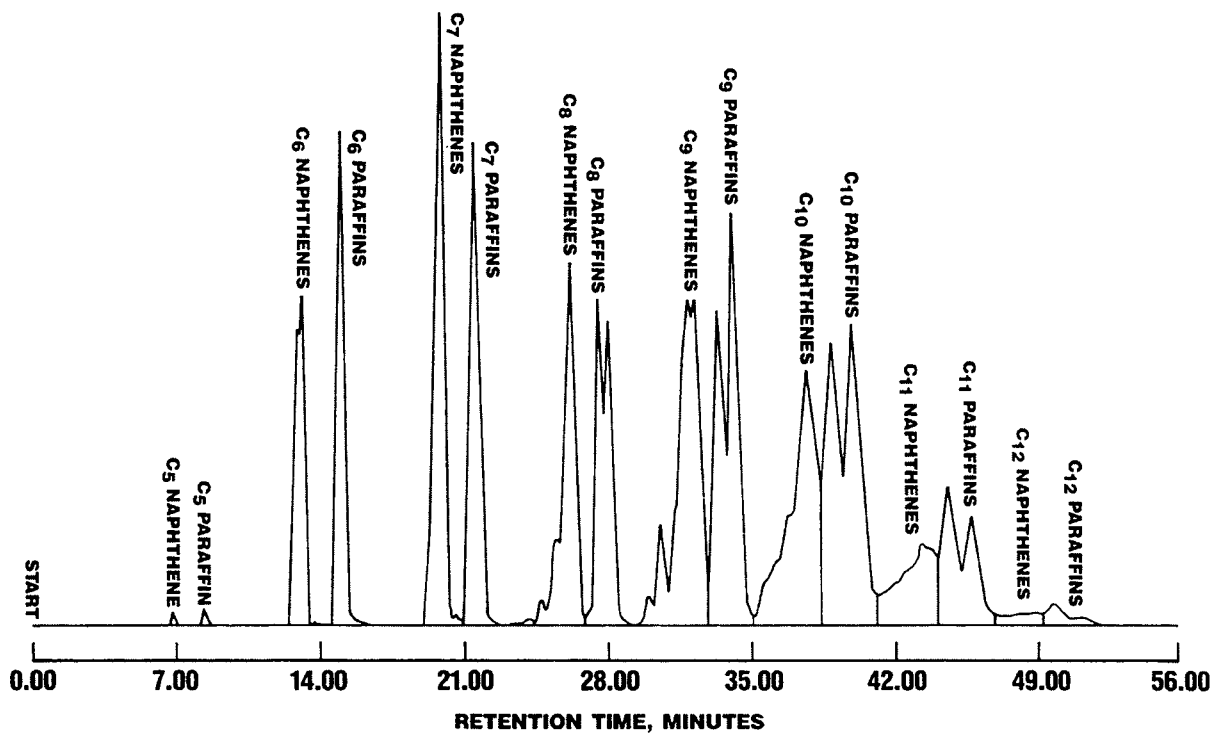


Figure 1
Typical Chromatogram
High Naphthene Sample

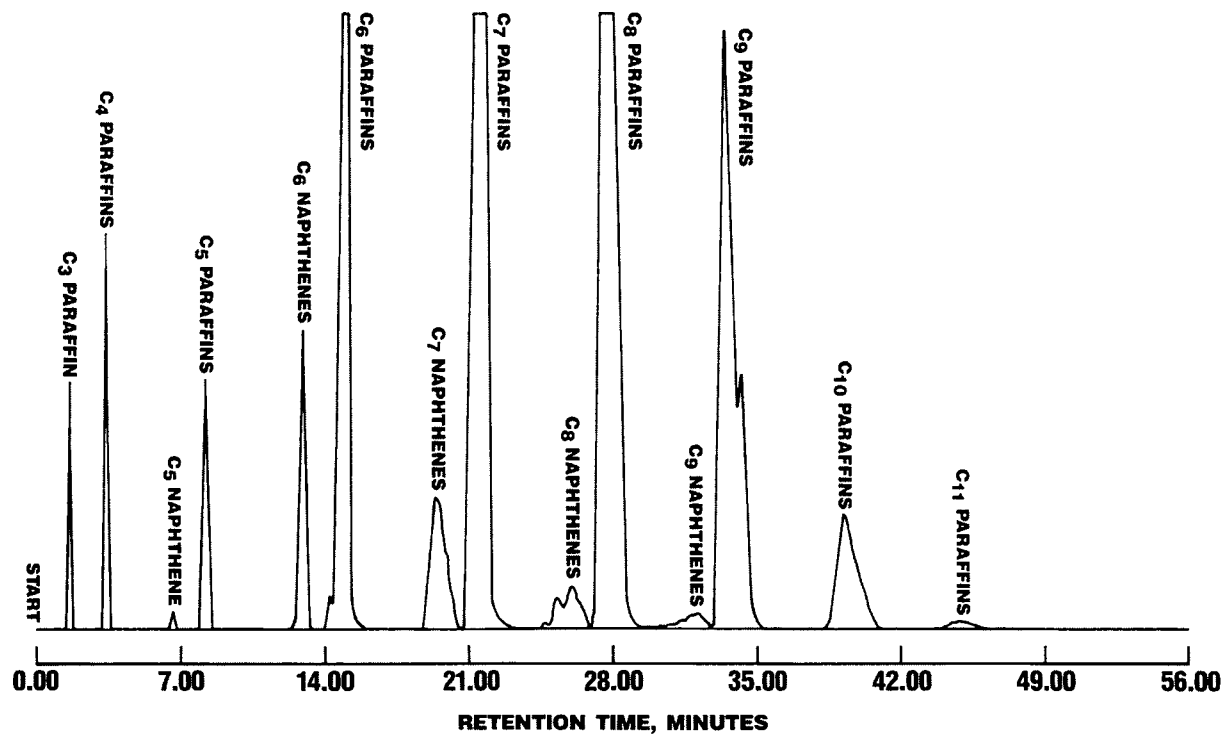


Figure 2

Typical Chromatogram
Low Naphthene Sample

Calibration

A calibration blend is required to relate the response of the various components to each other. Prepare a blend as described in ASTM Method D 4307 containing representative paraffin and naphthene components at approximately the concentrations expected in the samples. Analyze the blend in duplicate as described under *Chromatographic Technique* and determine the average area for each paraffin and naphthene peak. Calculate the mass response factor for each component relative to *n*-heptane as follows:

$$F = \frac{AB}{CD}$$

where:

A = component in blend, mass-%

B = area of *n*-heptane peak

C = *n*-heptane in blend, mass-%

D = area of component peak, units consistent with B

F = relative response factor for component (other than *n*-heptane)

Determine relative mass response factors as directed above for each instrument used. The factors shown in Table 2 are examples and will not be valid for all instruments.

Table 2

Typical Mass Response Factors

C₅ Naphthene	1.02
C₅ Paraffin	1.02
C₆ Naphthene	1.00
C₆ Paraffin	1.03
C₇ Naphthene	0.98
C₇ Paraffin	1.00
C₈ Naphthene	0.99
C₈ Paraffin	0.98
C₉ Naphthene	0.98
C₉ Paraffin	0.99
C₁₀ Naphthene	0.98
C₁₀ Paraffin	0.99
C₁₁ Naphthene	0.96
C₁₁ Paraffin	0.97
C₁₂ Naphthene	0.99
C₁₂ Paraffin	0.99

CALCULATIONS

Calculate the concentration of each paraffin and naphthene by carbon number to the nearest 0.1 mass-%, using the following equation:

$$\text{Component, mass-\%} = \frac{100 \text{ EF}}{\text{S}}$$

where:

E = component peak area

F = relative response factor, previously defined

S = sum of the products, EF, of all the paraffin and naphthene peaks

100 = factor to convert to mass-%

To calculate liquid volume-percent, the relative mass response factor is adjusted for difference in relative density for each hydrocarbon group as follows:

$$\text{L} = \frac{\text{F}}{\text{M}}$$

where:

L = liquid volume response factor for component

F = relative mass response factor for component, previously defined

M = average relative density for hydrocarbon group (see Table 3)

Table 3

<u>Hydrocarbon group</u>	<u>Average Relative Density</u>
C₄ Paraffins	0.568
C₅ Naphthene	0.745
C₅ Paraffin	0.625
C₆ Naphthene	0.776
C₆ Paraffin	0.660
C₇ Naphthene	0.763
C₇ Paraffin	0.684
C₈ Naphthene	0.775
C₈ Paraffin	0.705
C₉ Naphthene	0.775
C₉ Paraffin	0.715
C₁₀ Naphthene	0.775
C₁₀ Paraffin	0.732
C₁₁ Naphthene	0.775
C₁₁ Paraffin	0.740
C₁₂ Naphthene	0.775
C₁₂ Paraffin	0.740

Calculate the LV-% concentration of each paraffin and naphthene group by carbon number as follows:

$$\text{Component, LV-\%} = \frac{100 \text{ EL}}{\text{P}}$$

where:

E = component peak area

L = relative liquid volume response factor, previously defined

P = sum of the products, EL, of all the paraffin and naphthene peaks

100 = factor to convert to LV-%

PRECISION

Based on five replicate determinations, the estimated standard deviation (esd) was calculated for the components listed in Table 4. Duplicate results by the same operator should not differ by more than the allowable difference indicated (95% probability).

Table 4

Component	Concentration, mass-%	esd, mass-%	Allowable Difference, mass-%
C₄ Paraffin	3.6	0.024	0.10
C₆ Naphthene	0.6	0.003	0.01
C₆ Paraffin	0.8	0.010	0.04
C₈ Naphthene	72.6	0.097	0.38
C₈ Paraffin	11.9	0.017	0.70
C₉ Paraffin	3.6	0.011	0.04

TIME FOR ANALYSIS

The elapsed time for one analysis is 1.0 hour. The labor required is 0.25 hour.

REFERENCE

ASTM Methods D 2002, D 2003 and D 4307, www.astm.org

SUGGESTED SUPPLIERS

Alltech Associates, Inc., 2051 Waukegan Rd., Deerfield, IL 60015

Analytical Controls Inc., 127 S. Washington, Naperville, IL 60540

Matheson, P.O. Box 96, Joliet, IL 60434

Wiley Organics, Inc., 4654 Kenny Road, Columbus, OH 43220